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PHONON SCATTERING IN GRAPHITE

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ABSTRACT

Effects on graphite thermal conductivities due to controlled alterations of the graphite structure by impurity addition, porosity, and neutron irradiation are shown to be consistent with the phonon-scattering formulation

$$1/\lambda = \sum_{i=1}^n 1/\lambda_i.$$

Observed temperature effects on these doped and irradiated graphites are also explained by this mechanism.

INTRODUCTION

A number of investigators¹⁻⁸ have had varying degrees of success in trying to analyze, in whole or in part, the mechanism of thermal conduction in graphites. Application of theory to experiment has been even less successful. One major reason has been use of data from experiments in which the variables were poorly controlled or in which extraneous variables were allowed to interfere with the observations. This report discusses, in terms of a simple phonon-scattering mechanism, the effects of carefully controlled impurity and defect additions, porosity, and temperature on measured thermal conductivities. There is strong evidence that graphite thermal conductivity behavior is consistent with this mechanism.

THEORY

The two major mechanisms by which heat is conducted in graphite are electronic motion and excitation of the acoustic modes in the graphite lattice. To a very good approximation, these mechanisms are

independent and the total thermal conductivity, λ , may be written as the sum of the components.

$$\lambda = \lambda_e + \lambda_L. \quad (1)$$

λ_L is commonly evaluated for metal systems by

$$\lambda_e = L\sigma T \quad (2)$$

(Weideman-Franz law), where T is the temperature; σ , the electrical conductivity; and L , the Lorentz function whose limiting value is 2.45×10^{-8} (V/degree)² for fully degenerate systems. Separation of the two thermal conductivity components for semiconductors is a little more involved. However, it may be done by altering the electrical conductivity (usually by doping the matrix material with small amounts of impurities that change the electron or hole concentration) and measuring λ as a function of σ . Since

$$\lambda = \lambda_L + L\sigma T, \quad (3)$$

a plot of λ vs σ extrapolated to $\sigma = 0$ permits determination of λ_L . This is, of course, true only for those

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rare systems in which the impurity addition does not affect λ_L . So far, efforts to distinguish between λ_L and λ_i in graphite by these and other methods have not been very successful.^{4,9-12} Here, this particular aspect of the problem is not treated. Instead, λ_L is considered without reference to λ_i , and, in this instance, the generality of the results seems unaffected by the omission. For graphite, the total observed thermal conductivity is given by Eq. (1); however, at room temperature (300 K) $\lambda_L > \lambda_i$ and the expression

$$\lambda = \lambda_L \quad (4)$$

although not exact, is a very reasonable approximation, as may be demonstrated by the following. Typical approximate values of λ and σ for a polycrystalline graphite at 300 K are about 150 W/m-K and 10^3 mho cm^{-1} , respectively. By Eq. (2), $\lambda_i \approx 0.735$ W/m-K and $\lambda_i/\lambda_L \approx 0.005$.

The lattice contribution to the thermal conductivity is limited by the various primary phonon scattering processes that can occur at crystallite boundaries, at defect or impurity sites of almost any kind, or as a result of phonon-phonon interaction (Umklapp processes). Generally, if a single mean free path, l , can be defined for each class of scatterer, it is proper to take the sum of the scattering probabilities to define the resultant mean path* as^{6,13}

$$\frac{1}{l} = \sum_{i=1}^n \frac{1}{l_i} \quad (5)$$

or, more specifically,

$$\frac{1}{l} = \frac{1}{l_B} + \frac{1}{l_U} + \frac{1}{l_D} \quad (6)$$

where

l_B = mean distance between crystallite boundaries,

l_U = mean free path for phonon-phonon scattering,

l_D = mean free path for (phonon) scattering by defects or impurities.

If the defect concentration is changed, the mean free path for defect scattering changes, $l_D \rightarrow l_D'$, $l \rightarrow l'$, and Eq. (6) becomes

**This is, in essence, Matthiessen's rule as applied to thermal resistance.*

$$\frac{1}{l'} = \frac{1}{l_B} + \frac{1}{l_U} + \frac{1}{l_D'} \quad (7)$$

If l_B and l_U are assumed to have remained constant, the ratio of resultant mean free paths may be determined by dividing Eq. (6) by Eq. (7) to get

$$\left(\frac{l'}{l} - 1\right) \left(\frac{l_D}{l_U} + \frac{l_D}{l_B}\right) + \frac{l'}{l} \frac{l_D}{l_D'} - 1 = 0 \quad (8)$$

and

$$\frac{l'}{l} = \frac{1 + A}{\frac{l_D}{l_U} + \frac{l_D}{l_B} + A} \quad (9)$$

where

$$A = \left(\frac{l_D}{l_U} + \frac{l_D}{l_B}\right) \quad (10)$$

As the test of the theory requires experiments in which only l_D , and thus l , may change, we must examine the validity of the assumptions about the constancy of l_B and l_U . Graphite has a hexagonal crystal structure with an extended a-b planar ring structure, and a 1.42-Å C-C bond length. The layer plane stacking is of the ABAB type with interplanar c-axis distances of 3.35 Å or more, depending on the degree of crystallinity of the graphite. The forces acting between the atoms in the a-b plane are due to strong covalent bonds, whereas those acting between the layer planes are of the weaker Van der Waals type. Because of this anisotropy in the structure, in-plane phonon processes are treated under the assumption that the layer planes are uncoupled.^{1,14} In fact, c-direction contributions can be ignored because of this uncoupling that permits one to consider only those processes that affect the properties in the in-plane direction, as is done here. Graphites are basically polycrystalline, and the mean distance between crystallite boundaries in the a-b direction corresponds to l_B (equal to the crystallographic L_a). This distance is a measurable crystallographic parameter, and the constancy of l_B may be ensured either by measurement (in going from one test specimen to another) or by changes induced in a single test sample, as by irradiation which can change the defect concentration without necessarily altering crystallite size.

The validity of the assumption that ℓ_U is constant cannot be established, so the concept expressed by Eq. (7) must be abandoned. The reasoning is as follows; past work on how irradiation influences the thermal conductivities of polycrystalline graphites^{11,15,16} and how boron impurity addition influences them¹² shows that near 300 K the total λ decreases with increased defect or impurity concentration. Irradiation decreases σ (electrical conductivity), whereas boron doping increases it. Thus the observed effect is clearly due to changes in λ_L and falls within the scope of this work. Since the thermal conductivity lattice component is related to the mean free path by the Debye relationship

$$\lambda_L = \frac{1}{3} \sum_{i=1}^n c_i v_i \ell_i, \quad (11)$$

where

C = heat capacity,

v = phonon velocity,

i = acoustic mode index,

and ℓ is given by Eq. (6), the observed effect on the thermal conductivity must be due to a lack of constancy in ℓ_U or ℓ_D or both, assuming that the constancy of ℓ_B has been established. Work at this Laboratory on effects of silicon doping in polycrystalline graphite, to concentration levels comparable with the boron work cited, showed essentially no change in λ or σ (see Table I). In this instance, a change in defect concentration affected neither ℓ_U nor ℓ_D (ℓ_B was constant). Therefore, it appears that the constancy of ℓ_U or ℓ_D as a function of defect concentration cannot be established *a priori* and, furthermore, that the two may not be separable. Probably the major ultimate effect of changing the defect concentration and thus introducing new scattering centers is altered periodicity of the potential field associated with the graphite structure which alters the value of ℓ_U . Perhaps it is more reasonable to rewrite Eq. (6) as

$$\frac{1}{\ell} = \frac{1}{\ell_B} + \frac{1}{\ell_U}, \quad (12)$$

where ℓ_U is understood to contain defect and impurity effects and where $\ell_U \rightarrow \ell_U'$ as the defect concentration is changed. As in Eqs. (7)-(9),

TABLE I

INFLUENCE OF SILICON ADDITION ON ELECTRICAL AND THERMAL PROPERTIES OF POLYCRYSTALLINE GRAPHITES

Silicon Content (at.%)	Electrical Resistivity ($\mu\Omega\text{-cm}$)	Thermal Conductivity (W/m-k)
C ^a	1131	130
0.019	1141	124
0.086	1146	126
0.252	1122	128

^a Pure graphite.

$$\frac{\lambda'}{\lambda} = \frac{\frac{1}{\ell_U} + F}{\frac{1}{\ell_U'} + F}, \quad (13)$$

where

$$F = \frac{\ell_U}{\ell_B}. \quad (14)$$

The similarity between Eqs. (9) and (13) is obvious and seems to be quite general for any number of variables treated as is done here. In other words, whether Eq. (6) contains two terms or n terms is immaterial, inasmuch as the final working equation is of the same form, and only the terms in the constant are different. Since ℓ_U' should decrease with increased defect concentration, ℓ_U/ℓ_U' should be proportional to impurity concentration, total radiation dosage, or any other variable that increases defect concentration. Also, the observed thermal conductivity will be directly proportional to λ' , Eq. (11), so a graph of λ vs defect concentration or exposure to radiation is similar to a plot of λ'/λ vs ℓ_U/ℓ_U' . Differentiating Eq. (13) gives

$$\frac{d(\lambda'/\lambda)}{d(\ell_U/\ell_U')} = - \frac{(1+F)^2}{\left(\frac{\ell_U}{\ell_U'} + F\right)^2}. \quad (15)$$

Since $\ell_U/\ell_U' > 0$, a plot of λ'/λ (or λ) vs ℓ_U/ℓ_U' (or defect concentration) always gives a concave curve with a

negative slope. This condition is general and, indeed, is characteristic of all curves of λ as a function of anything (temperature lattice defects due to irradiation, interstitials, porosity, residue compounds) that influences the phonon mean free path.

COMPARISON WITH EXPERIMENTS

Defect and Impurity Effects

Data for testing the ideas presented here are relatively scarce, because the requirement of L_a (i.e., f_B) constancy makes it mandatory that changes imposed upon a test specimen to alter its thermal conductivity be made either on a single specimen or on several specimens whose constant L_a value has been verified experimentally. Furthermore, for anisotropic systems (and graphite certainly fits in that category) evidence that the preferred orientation has remained constant during the doping or structural alteration is required, because orientation changes can cause thermal conductivity changes that can effectively mask the effects being investigated. Although reported measurements on similar "grades" or "batches" of graphites do not normally meet the standards set forth here, some literature data are considered here because the care used in the experiments approaches that required.

A group of experiments performed at this Laboratory on how boron doping affects polycrystalline graphite properties yielded information on thermal conductivity effects when L_a and the degree of preferred orientation were kept constant. These results are shown in Fig. 1, a plot of room-temperature thermal conductivities of boron-doped graphites vs boron content. The manufacture, crystallographic parameters, boron disposition, and effects on other properties of these graphites have been detailed.¹² Because the graphite was in the form of extruded rods, λ was measured parallel and perpendicular to the extrusion axis to show the effect of orientation. The upper curve in Fig. 1 reflects measurements made parallel to the extrusion axis; because the crystallite planes tend to align themselves along the extrusion axis, these λ values are higher than those perpendicular to the extrusion axis. The shapes of the curves in Fig. 1 are exactly those predicted from Eq. (15) which is based on the simple phonon-scattering model.

Smith and Rasor¹⁷ reported on how neutron irradiation and formation of bromine residue compounds affect graphite thermal conductivities. Although L_a measurements and pertinent crystallographic information were not included in their work, they were careful to ensure that the results

Fig. 1.

Effect of boron on the room temperature thermal conductivity of polycrystalline graphite. Measurements made parallel and perpendicular to the extrusion axis.

were not unduly influenced by variables other than those intended. These data are of particular interest because the neutron irradiation produces a severely defect-laden lattice whereas the bromine residue compounds have their greatest effect on the character of the crystallite boundaries, thus permitting more or less independent consideration of f_U and f_B effects. Smith and Rasor presented their data as plots of λ vs T with total neutron exposure or bromine content as an independent parameter. To show the effects pertinent to this work, some of their data are cross-plotted in Fig. 2 to show how integrated neutron flux affects the thermal conductivity (all measurements made at 100 K) of 3A-25 graphite. Recalling that λ varies as l^2 in the phonon-scattering model and f_U/f_B is proportional to total radiation exposure, we see that the expected concave curve of negative slope is generated when λ is plotted vs integrated flux in Fig. 2. These conclusions apply equally well to all of Smith and Rasor's data on neutron-irradiated graphites and to more recent results.¹⁷

Graphite and bromine residue compounds are made by allowing bromine to react with graphite to form unstable lamellar compounds and then heating

Fig. 2.

Effect of neutron irradiation on thermal conductivity (measured at 100 K) of SA-25 graphite. One MW-day equals 10^7 nvt neutrons with energy greater than 0.5 MeV.¹⁶

Fig. 3.

Effect of bromine content on thermal conductivity (measured at 100 K) of AGOT-KC graphite.¹⁶

the system and allowing the compounds to decompose. At all but extremely high temperatures ($> 2000^\circ\text{C}$), some of the bromine remains behind upon decomposition. Essentially all the remaining bromine resides in the crystallite boundaries and other discontinuities, thus making for a system in which only boundary scattering should be affected, neglecting electron processes. For the AGOT-KC graphite they used, Smith and Rasor estimated that a little more than 1 at.% of bromine was the most that could be accommodated without damaging the graphite crystallites. Bromine's effect on the thermal conductivity, at 100 K, of AGOT-KC graphite below this limiting concentration is shown in Fig. 3. Once again, the typical curve shape to be expected from the relation

$$\frac{\lambda'}{\lambda} = \frac{1 + \frac{\lambda_B}{\lambda_U}}{\frac{\lambda_B}{\lambda_U} + \frac{\lambda_B}{\lambda_U}} \quad (16)$$

is observed. In this instance, however, note that l_B is not actually changed in dimension; instead, it is the scattering efficiency of the crystallite boundary which has changed. This concept in the same context was discussed by Jamieson and Mrozowski³ who used a multiplicative factor, γ_B , to account for the phonon-scattering probability at the boundary. In their notation, $\gamma_B l_B$ would be equivalent to the l_B used here and changes in scattering efficiency would be reflected in changed values of γ_B .

High and Low Temperature Effects

At well below room temperature, l_U becomes large enough that $l = l_B$ in extreme cases and where single crystals are used l_B , and thus λ , is determined by the specimen size.¹⁸ With decreasing T , $l_U/l_B \gg 1$ and $l_U/l_B \gg l_U/l_U$ and Eq. (13) becomes

$$\frac{\lambda'}{\lambda} = \frac{1 + \frac{\lambda_U}{\lambda_B}}{\frac{\lambda_U}{\lambda_U} + \frac{\lambda_U}{\lambda_B}} + 1 \quad (17)$$

Thus, one would expect thermal conductivity curves for materials that are essentially identical, except for different defect concentrations, to converge with decreasing temperature, assuming of course that the maximum temperature considered is low enough so that l_U/l_B is either greater than or not too different from unity. Again, data for testing these ideas are scarce because of the required constant l_B and orientation. However, Powell and Wagner's work¹⁵ seems to fit this category and some of Smith and Rasor's data¹⁶ also can be considered. Powell and Wagner used three specimens of commercially available polycrystalline graphites and measured λ from 20 to about 100 K. They then irradiated the samples with neutrons and remeasured the thermal conductivity over the same temperature range. At 100 K, the conductivity was only about 15% of its preirradiation value; however, comparison of the irradiated specimens' λ vs T curves with those plotted before irradiation showed a convergence with decreasing temperature as Eq. (17) predicts. Smith

and Rasor's plots of λ vs T from 20 to about 300 K showed a similar behavior, in that increased neutron exposures led to greater differences in λ near room temperature and the thermal conductivities tended to converge with decreasing temperature. The same is true of their results with the graphite and bromine residue compounds. Thus the low temperature behavior analysis based on the phonon-scattering model seems reasonably well substantiated by experimental evidence, despite anticipation that, by analogy with the electrical properties from which Mathiessen's rule is derived, there would be some residual thermal resistivity at 0 K.

Above room temperature, the U processes become increasingly important. Generally l_U is proportional to $1/T$,^{19,20} and l_U/l_B decreases accordingly, whereas the ratio l_U/l'_U should remain fairly constant since both should go as $1/T$ at high temperatures. Then Eq. (13) becomes

$$\frac{\lambda'}{\lambda} = \frac{1 + \frac{l_U}{l_B}}{\frac{l_U}{l'_U} + \frac{l_U}{l_B}} \approx \frac{l'_U}{l_U} \quad (18)$$

Thus one would expect that λ'_j and λ , again equating λ with l of Eq. (11), plotted vs temperature for graphites that differ only in defect concentration (j) would show no tendency to converge even at the highest temperatures and would yield a series of curves. This postulate is exceedingly difficult to verify because of the scarcity of germane data. Wagner and Dickinson¹² published curves of λ vs T from about -100 to 2500°C for graphites containing small amounts of boron. Although these curves lie in the expected order (λ'_j decreases with increasing boron content as shown in Fig. 1) and there is no evidence to contradict Eq. (18), it is unfortunate that above 1500°C the relative errors in the radial heat flow measurement²¹ exceed the expected λ'_j differences between the curves. As no other data that fit the conditions on λ_B etc. are known, the high temperature analysis must be considered to lack firm experimental backing.

Miscellaneous Observations

It is of interest to consider the relative values of l_U and l_B . This may be done by evaluating Eq. (12) at the point where the thermal conductivity (plotted vs T) goes through a maximum, $d\lambda/dT = 0$, that for graphite is normally just above room temperature. If Eq. (12) is solved for l and differentiated with respect to temperature, allowing $d/dT = 0$,

$$l_U^2 \frac{\partial l_B}{\partial T} + l_B^2 \frac{\partial l_U}{\partial T} = 0. \quad (19)$$

Near the conductivity maximum, none of the above terms is zero and when

$$\frac{\partial l_B}{\partial T} = - \frac{\partial l_U}{\partial T},$$

$$l_U = l_B. \quad (20)$$

The above conclusion that at maximum thermal conductivity the boundary scattering is equal to the Umklapp scattering has appeared in the literature^{22,23} and is hardly startling. However, it is an interesting result in view of the assumption that there is no electronic contribution to the thermal conductivity and of the extremely simple mechanism implied by considering only two in-plane scattering processes.

Ivanov²⁴ has suggested that for porous materials (graphite porosity varies from near 0 to 50%) the resultant mean free path should be formulated as in Eq. (6)

$$\frac{1}{l} = \frac{1}{l_U} + \frac{1}{l_B} + \frac{1}{l_{\text{pores}}}. \quad (21)$$

where l_{pores} is a distance between pores. This suggestion was shown to be valid by the work of Wagner, O'Rourke, and Armstrong,²⁵ in which pore concentration was the experimental variable of interest. They used 15 graphite samples with 15-32% porosities. The crystallite heights, lattice spacing, anisotropies, and pore sizes and shapes were sensibly constant, and the primary variable was the number of pores. For these graphites, Ivanov's relation implies that

$$\begin{aligned} \lambda &\approx \frac{1}{l} \approx \frac{1}{l_{\text{pores}}} \approx \frac{1}{\text{number of pores}} \\ &\approx \frac{1}{\text{porosity}}. \end{aligned}$$

The data were plotted as $1/\lambda$ vs porosity and fitted a straight line. This is significant because density corrections to thermal conductivity in graphite have been difficult to apply, probably because conduction is associated with a scattering phenomenon rather than a simple Maxwellian area correction.

SUMMARY

The basic phonon-scattering formulation, Eq. (5), has been shown to be applicable for pyrolytic and polycrystalline graphites in various stages of imperfection and at various temperatures, with no alteration of the original premise. Although temperature effects seem to be reasonably well rationalized in this work, phonon-scattering efficiencies at the crystallite boundaries must be better defined. However, above all, better experiments with carefully controlled or identified structural parameters such as crystallite anisotropies, lattice spacings, and crystallite sizes are needed before any theory of heat conduction in graphite can be shown to correspond to reality.

The implications for more immediate applications are more obvious and concern the formulation for the overall thermal conductivity or multiphase systems. Past custom has been to express thermal conductivities of multiphase systems as combinations of the form

$$\lambda = \sum_{i=1}^n a_i \lambda_i$$

or

$$\lambda^{-1} = \sum_{i=1}^n a_i (\lambda_i)^{-1}.$$

The reasons for favoring one form more than the other have never been defined clearly, so both types of expressions have appeared in the literature. Taking graphite as a limiting case of a multiphase system (the pore structure being the second phase), it appears that the second type of expression is quite reasonable, as this work shows. Furthermore, since interfacial boundaries in a multiphase system will act as phonon scatterers, there is reason to use the expression

$$\frac{1}{\lambda} = \sum_{i=1}^n \frac{a_i}{\lambda_i} \quad (22)$$

for systems in which phonon propagation plays a major role in heat conduction.

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